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Simple Halogen Derivatives of Acetylene

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IN 1861 Sawitsch and Reboul (1) prepared compounds which could be represented by formulas such as C_2HCl and C_2Cl_2 . Before 1890 many such halogen substitution products of acetylene had been prepared, and it was known that most of them were poisonous and explosive or spontaneously inflammable in air, and had sharp odors like phosphine or phosgene. About 1897 Nef (2), contrasting the mono- and dihalogen compounds with the more harmless and stable methyl- and dimethylacetylenes, $CH:CCH_3$ and $CCH_3:CCH_3$, proposed the acetylidene structure for halogen compounds: $CHX:C<$ and $CX_2:C<$.

The conception of divalent carbon advanced by Nef and Lawrie (3) seemed to explain some of the properties of the halogenated acetylene derivatives. Studies of carbon monoxide, with its divalent carbon and great affinity for oxygen, formed the basis for the acetylidene structure hypothesis. Many derivatives in which two halogen atoms were attached to the same carbon atom were prepared in attempts to establish the acetylidene structure. For instance, dibromiodoethylene was formed by the addition of hydrogen iodide to C_2Br_2 , produced by treating tribromoethylene with alcoholic potassium hydroxide. By oxidation of the dibromiodoethylene

with fuming nitric acid, iodine and dibromoacetic acid were obtained.

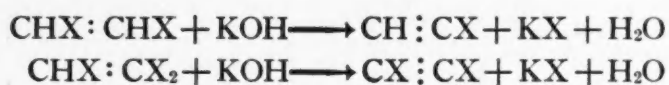
After a period of some controversy, the hypothesis of the acetylidene structure gained ground and was published in textbooks. It seemed to have been generally accepted when Biltz in 1913 published a paper (4) in which he attacked the conclusions of Nef and Lawrie on the ground that derivatives having two halogen atoms on the same carbon atom could be produced from symmetrical dihalogen-substituted acetylenes. This is brought about through a mechanism of "oxidation rearrangement" analogous to the pinacolone rearrangement.

In 1930 it was recognized by Straus, Kollek, and Heyn (5), who had produced many new halogen substitution derivatives of acetylene and diacetylene, that the question of structure of these compounds had not been settled. In 1935 de Laszlo (6) measured the carbon-halogen link distances in dibromoacetylene and diiodoacetylene. He used a new electron-diffraction method. His measurements were 1.84 Å. for C-Br and 2.03 Å. for C-I—distances shorter than those found for carbon-halogen linkages in di- and tetrabromoethylenes (1.91 Å.) and in di- and tetraiodoethylenes (2.10 Å.). This is a good indication that the halogens in the acetylene derivatives are linked to carbon-carbon triple bonds. In

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1941 Finbak and Hassel (7) made physical measurements of dichloroacetylene by Debye's rotating sector method of electron interference. They found it to be a linear symmetrical molecule in which the C-C bond distance is 1.195 Å. and the C-Cl bond distance is 1.640 Å., definitely proving that the compound is not an acetylidene.

Among the methods by which halogen substitution products of acetylene may be formed, the one used by Sawitsch and Reboul (1) is probably of most general interest to the organic chemist. This is the well-known reaction of a di- or tri-halogen ethylene with alkali:



Ott, Ottemeyer, and Packendorff (8) showed that dichloroacetylene, a liquid which boils at 32°C., could be prepared by distilling trichloroethylene at 130°C. (in an atmosphere free from oxygen) through solid granulated potassium hydroxide previously dehydrated so that it would solidify at about 200°C. If pure caustic potash was used, violent explosions occurred. Explosions were prevented by using impure potassium hydroxide, or by adding a small proportion (less than one per cent) of a silicate to pure potassium hydroxide. No satisfactory explanation has yet been proposed to account for the moderating influence of this small concentration of silicate upon the behaviour of the halogen-substituted acetylene produced. However, dichloroacetylene obtained with potash contaminated by a silicate does ignite spontaneously in air, and has the physical properties normally attributed to this compound.

Dichloroacetylene may also be formed by heating barium trichloroacrylate. Monochloroacetylene, a gas boiling at -31°C., is a decomposition product of the dichloroacrylate. Diiodoacetylene, which melts at 80°C., may be produced by reaction of iodine and acetylene. The method is not suitable for preparing

other halogen-substituted acetylenes because addition products are formed.

In 1932 Nieuwland and Vaughn (9) prepared diiodoacetylene by the reaction of iodine and acetylene in liquid ammonia. Vaughn later prepared the same compound by the reaction of iodine and calcium carbide in liquid ammonia.

Straus, Kollek, and Heyn (5) discovered that halogen-substituted acetylenes could be formed by the reaction of acetylene or some of its derivatives with alkaline hypohalogenite solutions:



They patented the process and produced a large number of compounds which they found to be of interest as drugs valuable for various pharmacological properties—many as soporifics or narcotics. Among these compounds were chloro- and bromophenylacetylene, dichlorodiacetylene, and a series of dialkylhalogenacetylenyl carbinols, $\text{RR}'\text{C}(\text{OH})\text{C:CX}$. Their method of preparation of these carbinols is especially valuable because the hydroxyl group interferes with utilization of most other methods, such as the use of a Grignard procedure. In the table on the following page are some of the members of this series of compounds.

During the era when acetylene was used for lighting purposes, explosions sometimes occurred while the acetylene was being purified by washing with hypochlorite solution; these explosions are now believed to have been caused by the formation of dichloroacetylene.

It is interesting to note that, although dichloroacetylene may be formed from caustic potash and trichloroethylene, an old process by which sym-tetrachloroethane reacts with aqueous alkali to form trichloroethylene is still one of the most important commercial procedures for making this chlorinated solvent. The boiling points of sym-tetrachloroethane, trichloroethylene, and dichloroacetylene are respectively 146°, 87°, and 32°C. Fortunately, dichloroacetylene is formed quite slowly by the reaction of trichloro-

ACETENYL CARBINOLS FORMED BY REACTION OF TERTIARY
ACETYLENE ALCOHOLS WITH HYPOHALOGENITE SALTS

Compound	Formula	Boiling Point
Dimethylbromoacetenyl carbinol	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}:\text{CBr}$	68° (15 mm.)
Methylethylbromoacetenyl carbinol	$(\text{CH}_3)(\text{C}_2\text{H}_5)\text{C}(\text{OH})\text{C}:\text{CBr}$	77° (15 mm.)
Diethylbromoacetenyl carbinol	$(\text{C}_2\text{H}_5)_2\text{C}(\text{OH})\text{C}:\text{CBr}$	87° (15 mm.)
Methyl tertiary butylbromoacetenyl carbinol	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{OH})\text{C}:\text{CBr} \\ \diagup \\ (\text{CH}_3)_3\text{C} \end{array}$	44° (11 mm.)
Bromoacetenylcyclohexanol	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \qquad \text{C} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{C}:\text{CBr} \end{array} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array}$	114° (12 mm.)
Chlorine compound corresponding to the preceding structure.		98° (13 mm.)

ethylene with aqueous alkali.

The greatest danger connected with the labile halogen-substituted acetylenes is that they may be formed inadvertently through lack of knowledge of the possibility of their formation. An example of this type of hazard occurred in a large solvent recovery plant last year. Crude acetone was being distilled from a mixture of the solvent with aqueous caustic soda, normally used in the process to remove certain impurities in the acetone. It was not known that the acetone had been contaminated with trichloroethylene. A small amount of dichloroacetylene was formed and was absorbed in acetone as the solvent condensed. Fortunately, the concentration of dichloroacetylene was so small that it ignited spontaneously only when portions of the distillate were

mixed with water (which removed the acetone, leaving the acetylene derivative on the surface), and no serious fire or explosion occurred.

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A Stillhead Suitable for the Preparation of Esters

THE reaction of an acid and an alcohol to form an ester and water is a common organic synthesis. In order to complete this reaction, it is necessary to remove one of the constituents, usually water, from the mixture by chemical or physical means. The most common physical

means is distillation. A fractionating column is a desirable aid for this process. Two such columns have previously been described in *Synthetic Organic Chemicals*; namely, in Vol. 9, No. 3 (1936) and Vol. 11, No. 1 (1938).

To reduce the amount of the lower-

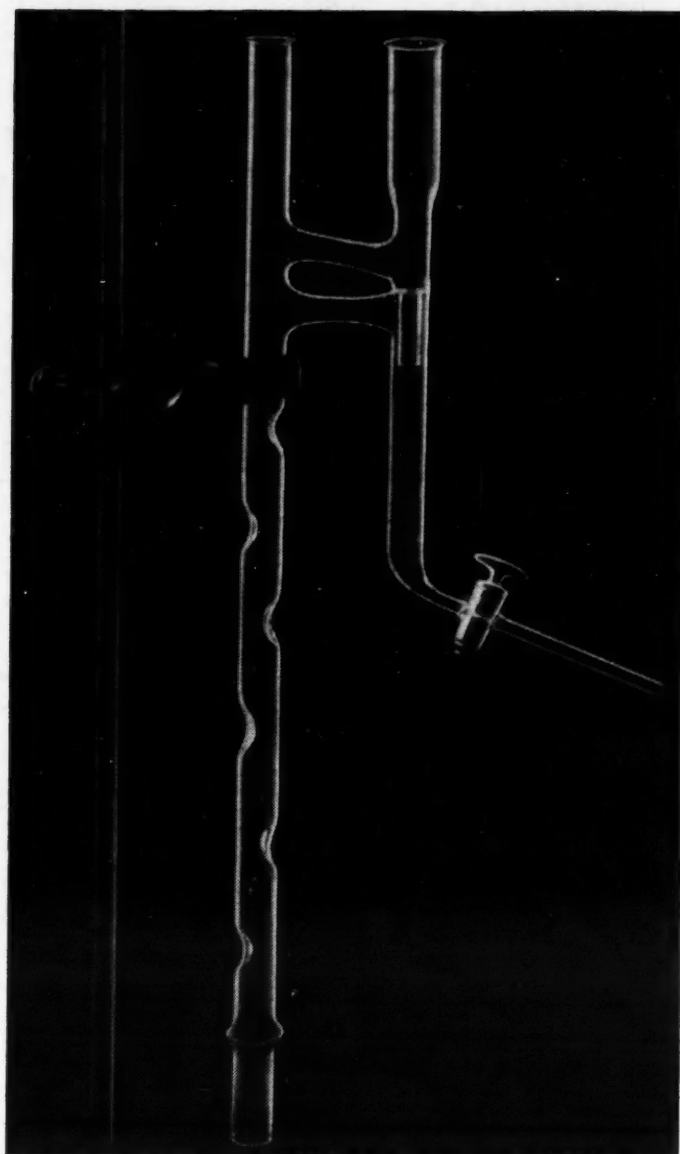
boiling reactant, the time of esterification, and the temperature of the reaction, a water-immiscible solvent such as benzene, toluene, carbon tetrachloride, etc., is added to the mixture. In practice a binary or ternary mixture is vaporized as the lowest boiling constituent of the esterification reaction. On condensing this vapor, two layers are formed, one of which is aqueous. Continued distillation would, therefore, complete the reaction by entire removal of the water. The proportion of water in the condensate may be very small, however, and to avoid the use of large volumes of solvent, methods have been devised to return the nonaqueous layer to the column or to the reaction mixture. For this purpose a stillhead has been constructed as part of a simple Vigreux-type column, as shown in the accompanying illustration. This column is designed for use with water-immiscible solvents which are lighter than the aqueous layer. A slight modification of the stillhead is necessary for use with heavy solvents.

Vapors from the column pass through the upper connecting tube to a reflux condenser. The vapors condense and drop into the side arm. Here they separate by gravity, and the light, nonaqueous portion returns to the column through the lower connecting tube. The bottom layer, or water, is drawn off through the stopcock as necessary. A baffle opposite the lower return tube prevents the return of water droplets from the splash-agitated liquid.

The column illustrated is about one meter long and 35 mm. in diameter. It has been used successfully for the preparation of several alkyl halides such as butyl and amyl bromides. High-boiling esters such as amyl acetates, phthalates, salicylates, and synthetic fats such as tripalmitin and trimyristin have been prepared. In the last two cases mentioned, xylene is used to aid in the removal of water.

A characteristic use of this type of column is in the preparation of n-amyl

phthalate. The excess amyl alcohol is the water-carrying agent. The following materials—10,560 g. n-amyl alcohol (120 moles), 7500 g. phthalic acid (45.2 moles), and 25 g. p-toluenesulfonic acid—are mixed in a 22-liter flask, which is heated about 24 hours over a steam bath with mechanical stirring until all the solid phthalic acid has gone into solution. The mixture is then refluxed over a free flame (without any mechanical stirring), using the column as already described. About 1400 cc. of water is collected; this requires 20 hours. The reaction mixture is allowed to cool, and is then neutralized with a weak solution of potassium carbonate. The ester layer is washed with water, and distilled under reduced pressure. The boiling point is 204-206°C. at a pressure of 10 mm. The yield is 12,900 g. of n-amyl phthalate, which is 93% of the theoretical amount, 13,830 g.



Modified Vigreux-type column

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